

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 December 2003 (24.12.2003)

PCT

(10) International Publication Number  
**WO 03/106346 A1**

(51) International Patent Classification<sup>7</sup>: C02F 1/04,  
3/00, 3/02, 9/00

(21) International Application Number: PCT/ZA03/00080

(22) International Filing Date: 18 June 2003 (18.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/390,689 18 June 2002 (18.06.2002) US  
2002/4849 18 June 2002 (18.06.2002) ZA

(71) Applicant (for all designated States except US): SASOL  
TECHNOLOGY (PTY) LTD [ZA/ZA]; 1 Sturdee Av-  
enue, Rosebank, 2196 Johannesburg (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DANCUART  
KOHLER, Luis, Pablo, Fidel [ZA/ZA]; 20 Lombard  
Street, 1947 Vaalpark (ZA). DU PLESSIS, Gert, Hen-  
drik [ZA/ZA]; 15 Vermeer Street, 2302 Secunda (ZA).  
DU TOIT, Francois, Jacobus [ZA/ZA]; 11 Culemborg

Street, 1947 Sasolburg (ZA). KOPER, Edward, Ludovi-  
cus [ZA/ZA]; 11 Douglas Street, 2302 Secunda (ZA).  
PHILLIPS, Trevor, David [ZA/ZA]; 53 Macowen Street  
-SE2, 1911 Vanderbijlpark (ZA). VAN DER WALT,  
Janette [ZA/ZA]; Gleneden 39, Constantia Avenue, 1947  
Vaalpark (ZA).

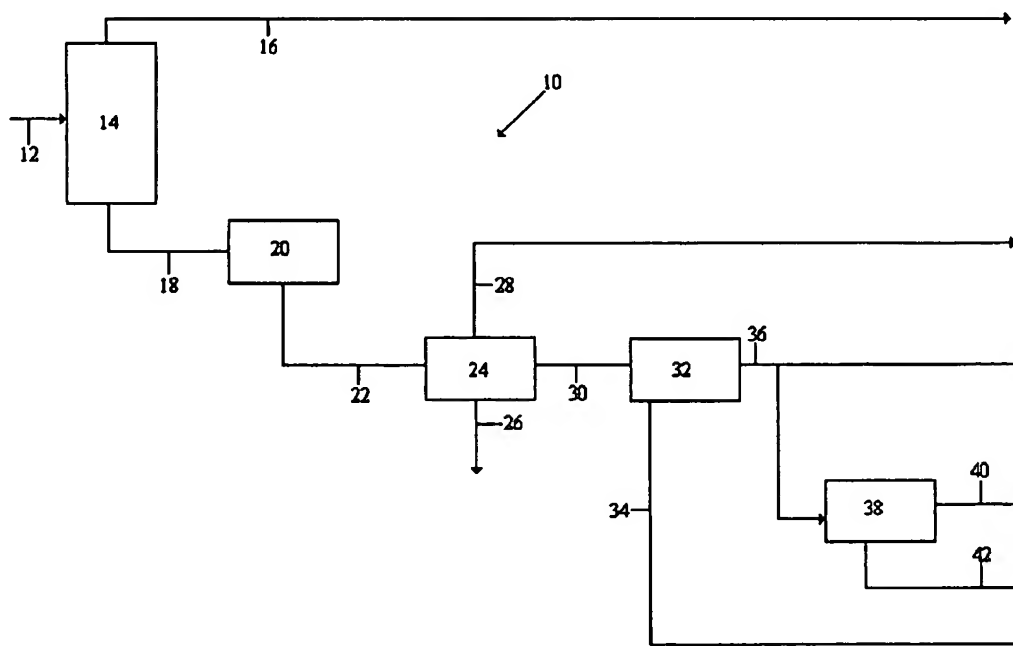
(74) Agent: HAHN & HAHN INC. LUTEREK, JF;  
WILLIAMS, VC; HAHN, HH, DUNLOP, AJS;  
MICHAEL, C; VENTER,; Hahn Forum, 222 Richard  
Street, 0083 Pretoria (ZA).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,  
SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG,  
US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,

[Continued on next page]

(54) Title: METHOD OF PURIFYING FISCHER-TROPSCH DERIVED WATER



(57) Abstract: A process for the production of highly purified water 40 from Fischer-Tropsch reaction water 12 includes distillation 14 as a primary treatment stage, evaporation 20 as a secondary treatment stage, aerobic treatment 24 as a tertiary treatment stage, solid-liquid separation 32 as a quartic treatment stage and membrane separation 38 as a final treatment stage.

WO 03/106346 A1



ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments*

**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

## **METHOD OF PURIFYING FISCHER-TROPSCH DERIVED WATER**

### **Field of the Invention**

- 5     This invention relates to the purification of water produced during Fischer-Tropsch synthesis for which synthesis a variety of carbonaceous materials are used as feedstock.

### **Background to the Invention**

10

The applicant is aware of processes for the synthesis of water from a carbonaceous feedstock, such as natural gas and coal, which processes also produce hydrocarbons.

- 15     One such process is the Fischer-Tropsch process of which the largest product is water and, to a lesser extent, hydrocarbons including olefins, paraffins, waxes, and oxygenates. There are numerous references to this process such as, for example on pages 265 to 278 of "Technology of the Fischer-Tropsch process" by Mark Dry, Catal. Rev. Sci.Eng., Volume 23 (1&2), 1981.

20

The products from the Fischer-Tropsch process may be processed further, for example by hydroprocessing, to produce products including synthetic crude oil, olefins, solvents, lubricating, industrial or medicinal oil, waxy hydrocarbons, nitrogen and oxygen containing compounds, motor gasoline, diesel fuel, jet fuel  
25     and kerosene. Lubricating oil includes automotive, jet, turbine and metal working oils. Industrial oil includes well drilling fluids, agricultural oils and heat transfer fluids.

- 30     In certain areas where carbonaceous feedstocks are to be found, water is in short supply and a relatively costly commodity. Also, environmental concerns prevent the disposal of polluted water derived from the Fischer-Tropsch process

into natural water ways and the sea thereby presenting a case for the production and recovery of useable water at the source of the carbonaceous feedstocks.

5 The carbonaceous feedstocks typically include coal and natural gas that are converted to hydrocarbons, water and carbon dioxide during Fischer-Tropsch synthesis. Naturally, other carbonaceous feedstocks such as, for example, methane hydrates found in marine deposits, can also be used.

10 Before the water produced during the Fischer-Tropsch process is purified in accordance with the present invention, it is typically subjected to preliminary separation aimed at isolating a water-enriched stream from the Fischer-Tropsch products.

15 The preliminary separation process includes condensing the gaseous product from the Fischer-Tropsch reactor and separating it in a typical three-phase separator. The three streams exiting the separator are: a tail gas, a hydrocarbon condensate including mainly hydrocarbons in the C<sub>5</sub> to C<sub>20</sub> range and a reaction water stream containing non-acid chemicals, water, acids, and suspended hydrocarbons.

20

The reaction water stream is then separated using a coalescer that separates the reaction water stream into a hydrocarbon suspension and a water-rich stream.

25 The coalescer is capable of removing hydrocarbons from the reaction water stream to a concentration of between 10 ppm and 1000 ppm, typically 50 ppm.

The water-enriched stream thus obtained forms the feedstock for the method according to the present invention and will be denoted in this specification by the term "Fischer-Tropsch reaction water".

30

The composition of the water-enriched stream or reaction water is largely dependent on the catalyst metal used in the Fischer-Tropsch reactor and the reaction conditions (e.g. temperature, pressure) employed. The Fischer-Tropsch reaction water can contain oxygenated hydrocarbons including aliphatic, aromatic and cyclic alcohols, aldehydes, ketones and acids, and to a lesser extent aliphatic, aromatic and cyclic hydrocarbons such as olefins and paraffins.

The Fischer-Tropsch reaction water may also contain small quantities of inorganic compounds including metals from the Fischer-Tropsch reactor, as well as nitrogen and sulphur containing species that originate from the feedstock.

The influence of the type of Fischer-Tropsch synthesis used on the quality of Fischer-Tropsch reaction water is illustrated in typical organic analysis (Table 1) of Fischer-Tropsch reaction water generated from three different synthesis operating modes, namely:

- Low Temperature Fischer-Tropsch                      LTFT                      Cobalt or Iron catalysts
- High Temperature Fischer-Tropsch                      HTFT                      Iron catalyst

Table 1: Typical Organic Composition of Fischer-Tropsch reaction water from Different Fischer-Tropsch Synthesis Operating Modes

Component (mass %)	LTFT (Cobalt Catalyst)	LTFT (Iron Catalyst)	HTFT (Iron Catalyst)
Water	98.89	95.70	94.11
non-acid oxygenated hydrocarbons	1.00	3.57	4.47
Acidic oxygenated hydrocarbons	0.09	0.71	1.41
Other Hydrocarbons	0.02	0.02	0.02
Inorganic components	< 0.005	< 0.005	< 0.005

It is evident from the typical analyses of Fischer-Tropsch reaction waters of different origin (Table 1) that these waters, in particular HT Fischer-Tropsch

reaction water, contain relatively high concentrations of organic compounds, and direct application or disposal of these waters is generally not feasible without further treatment to remove undesirable constituents. The degree of treatment of the Fischer-Tropsch reaction water depends largely on the intended application, and it is possible to produce a wide range of water qualities ranging from boiler feed water to partially treated water which may be suitable for discharge to the environment.

It is also possible to co-treat Fischer-Tropsch reaction water with other typical process waste water as well as rain water.

The water purification processes described in this invention may, after making minor adaptations, also be used for the processing of aqueous streams derived from generic synthesis gas conversion processes using metallic catalysts similar to the catalysts used during Fischer-Tropsch synthesis.

### **Summary of the Invention**

According to a first aspect of the invention there is provided a process for the production of purified water from Fischer-Tropsch reaction water, which process includes at least the steps of:-

- a) a primary treatment stage comprising an equilibrium staged separation process having at least one stage for removing at least a fraction of non-acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
- b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby to reduce the total mass fraction of organic constituents in the unevaporated portion to produce a secondary water-enriched stream; and

- c) a final treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the secondary water-enriched stream.

5        According to a second aspect of the invention there is provided a process for the production of purified water from Fischer-Tropsch reaction water, which process includes at least the steps of:-

- (a) a primary treatment stage comprising an equilibrium stage separation process having at least one stage for removing at least a fraction of non-  
10        acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
- (b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby to reduce the total mass fraction of organic constituents in the unevaporated portion to produce a  
15        secondary water-enriched stream;
- (c) a tertiary treatment stage comprising biological treatment for removing at least a fraction of dissolved organic carbon from the secondary water-enriched stream to produce a tertiary water-enriched stream; and
- d) a quartic treatment stage comprising solid-liquid separation for removing  
20        at least some solids from at least a portion of the tertiary water-enriched stream.

The term "purified water" is to be interpreted as meaning an aqueous stream having a COD of between 20 and 500 mg/l, a pH of between 6,0 and 9,0, a  
25        suspended solids content of less than 250 mg/l and a total dissolved solids content of less than 600 mg/l.

The non-acid oxygenated hydrocarbons are typically selected from the group including: alcohols, ketones and aldehydes, and are more specifically selected  
30        from the group including: acetaldehyde, propionaldehyde, butyraldehyde,

acetone, methyl-propyl-ketone, methanol, ethanol, propanol, butanol, pentanol, hexanol, and heptanol.

5 A number of equilibrium staged separation processes are suitable for use in the primary treatment stage. Such processes may include conventional distillation processes typically used in the refining and petrochemical industry as well as solvent extraction using either conventional liquid solvents or liquefied gases.

10 When distillation is used as the primary treatment stage, the bulk of the non-acid oxygenated hydrocarbons contained in the Fischer-Tropsch reaction water are removed, leaving predominantly mono-carboxylic acids (e.g. acetic acid, propionic acid) and optionally trace quantities of non-acid compounds. As a result of the presence of organic acids, the primary water-enriched stream is known as Fischer- Tropsch acid water.

15 The overheads from distillation may be recovered and worked-up to products, or may be used for fuel or as an energy source.

20 The primary treatment stage may include degassing of the reaction water before further processing to remove compounds having a very low boiling point and dissolved gases from the Fischer-Tropsch reaction water.

25 Typically, Fischer-Tropsch reaction water originating from HTFT iron catalyst processes which water has undergone primary treatment has limited application due to the relatively high concentrations (> 1% by mass) of organic acids remaining in the FT acid water and further treatment of the water is required. In contrast, Fischer-Tropsch reaction water originating from cobalt-based LTFT processes which water has undergone primary treatment contains significantly lower organic acid concentrations (< 0.1 % mass %) and can therefore, following  
30 neutralization, be released to the environment if sufficient dilution is available and



discharge standards permit. The primary water-enriched stream may also have limited application as process water.

5 The evaporation in step b) may take place at ambient temperature and pressure in a cooling tower.

During evaporation in the cooling tower, the amount of at least some of the dissolved organic constituents contained in the primary water-enriched stream are reduced through the action of micro-organisms. The constituents being  
10 removed totally or partially include acidic oxygenated hydrocarbons and methanol.

By using the primary water-enriched stream as cooling water, the abundance of oxygen caused by aeration in the cooling tower activates the growth of micro-organisms that use dissolved organic constituents in the primary water-enriched  
15 stream as food source.

The evaporation may comprise use of the primary water-enriched stream as make up water to an evaporative cooling tower. The evaporative cooling tower  
20 may be selected from the group including: mechanical-draft cooling towers, natural-draft cooling towers and forced-draft cooling towers.

When using the primary water-enriched stream as cooling water, the linear flow velocity of said water through the equipment being used in the cooling must be  
25 sufficiently high enough to inhibit deposition of suspended solids in said equipment.

The pH of the primary water-enriched stream should be controlled by addition of an alkali, such as caustic soda, to prevent acid corrosion of metal and/or  
30 concrete surfaces that might be exposed to this water.

One or more suitable additives may be added to the primary water-enriched stream before using it as cooling water to inhibit undesirable effects such as, for example, fouling, corrosion and scaling.

- 5    Biological treatment of the secondary water-enriched stream may include aerobic treatment.

The aerobic treatment method may be the same as is conventionally used for domestic and industrial wastewater treatment.

10

The aerobic treatment may include adding nutrients in the form of nitrogen (e.g. urea, ammonia or ammonium salts) and phosphorus (e.g. phosphate salts) containing compounds to accelerate microbiological degradation of the organic carbon-containing constituents. In addition, pH control using alkali compounds  
15    such as lime, caustic and soda ash may be required to optimize the performance of the micro-organisms.

A wide range of technologies may be used in the aerobic treatment of the secondary water-enriched stream. Such technologies may be selected from a  
20    group including: Activated Sludge processes, High-rate Compact Reactors, Biological Aerated Filters, Trickling filters, Rotating Biological Contactors, Membrane Bioreactors and Fluidised Bed reactors. The aerobic production of Single Cell Protein (SCP) has also been successfully developed.

25    Apart from a water-rich or tertiary water-enriched stream, aerobic treatment typically yields carbon dioxide and sludge as byproducts. The carbon dioxide may be released to the environment. The sludge may be incinerated, used as land fill, fertilizer, soil conditioner or as a source of SCP.

30    The quartic treatment stage may be aimed at removing suspended solids from the tertiary water-enriched stream produced during biological treatment.

Suspended solid removal may be achieved by methods selected from the group including: sand filtration, membrane separation (e.g. micro- or ultrafiltration), flocculation sedimentation, dissolved air flotation (with or without the use of flocculants) and centrifugation.

5

Local discharge standards or the intended application will dictate the required level and type of quartic treatment.

Applications for the purified water produced by the method described above may include its use as cooling water, irrigation water or general process water.

10

The purified water typically has the following characteristics:

Property		
Chemical Oxygen Demand (COD)	mg/l	20- 500
pH		6,0- 9,0
Total Dissolved Solids (TDS)	mg/l	<600
Suspended solids (SS)	mg/l	<250

According to a third aspect of the invention there is provided a process for the production of highly purified water from Fischer-Tropsch reaction water, which process includes at least the steps of:-

15

- a) a primary treatment stage comprising an equilibrium staged separation process having at least one stage for removing at least a fraction of non-acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
- b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby to reduce the total mass fraction of organic constituents in the unevaporated portion to produce a secondary water-enriched stream;

20

25

- c) a tertiary treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the secondary water-enriched stream, to produce a tertiary water-enriched stream; and
- (d) a quartic treatment stage comprising a dissolved salt and organic removal stage for removing at least some dissolved salts and organic constituents from at least a portion of the tertiary water enriched stream.

According to a fourth aspect of the invention there is provided a process for the production of highly purified water from Fischer-Tropsch reaction water, which process includes at least the steps of:-

- a) a primary treatment stage comprising an equilibrium stage separation process having at least one stage for removing at least a fraction of non-acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
- b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby to reduce the total mass fraction of organic constituents in the unevaporated portion to produce a secondary water-enriched stream;
- c) a tertiary treatment stage comprising biological treatment for removing at least a fraction of dissolved organic carbon from the secondary water-enriched stream to produce a tertiary water-enriched stream;
- d) a quartic treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the tertiary water-enriched stream to produce a quartic water-enriched stream; and
- e) a final treatment stage comprising a dissolved salt and organic removal stage for removing at least some dissolved salts and organic constituents from at least a portion of the quartic water enriched stream.

The term "highly purified water" is to be interpreted as meaning an aqueous stream having a COD of less than 50 mg/l, a pH of between 6,0 and 9,0, a

suspended solids content of less than 50 mg/l and a total dissolved solids content of less than 100 mg/l.

5 | The non-acid oxygenated hydrocarbons are typically selected from the group including: aldehydes, ketones and alcohols, and are more specifically selected from the group including: acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl-propyl-ketone, methanol, ethanol, propanol, butanol, pentanol, hexanol, and heptanol.

10 | A number of equilibrium staged separation processes are suitable for use in the primary treatment stage. Such processes may include conventional distillation processes typically used in the refining and petrochemical industry as well as solvent extraction using either conventional liquid solvents or liquefied gases.

15 | When distillation is used as the primary treatment stage, the bulk of the non-acid oxygenated hydrocarbons contained in the Fischer-Tropsch reaction water are removed, leaving predominantly mono-carboxylic acids (e.g. acetic acid, propionic acid) and optionally trace quantities of non-acid compounds. As a result of the presence of organic acids, the primary water-enriched stream is known as  
20 | Fischer- Tropsch acid water.

The overheads from distillation may be recovered and worked-up to products, or may be used for fuel or as an energy source.

25 | The primary treatment stage may include degassing of the reaction water before further processing to remove compounds having a very low boiling point and dissolved gases from the Fischer-Tropsch reaction water.

Typically, Fischer-Tropsch reaction water originating from HTFT iron catalyst  
30 | processes which water has undergone primary treatment has limited application due to the relatively high concentrations (> 1% by mass) of organic acids

remaining in the FT acid water and further treatment of the water is required. In contrast, Fischer-Tropsch reaction water originating from cobalt-based LTFT processes which water has undergone primary treatment contains significantly lower organic acid concentrations ( $< 0.1$  % mass %) and can therefore, following  
5 neutralization, be released to the environment if sufficient dilution is available and discharge standards permit. The primary water-enriched stream may also have limited application as process water.

The evaporation in step b) may take place at ambient temperature and pressure  
10 in a cooling tower.

During evaporation in the cooling tower, the amount of at least some of the dissolved organic constituents contained in the primary water-enriched stream are reduced through the action of micro-organisms. The constituents being  
15 removed totally or partially include acidic oxygenated hydrocarbons and methanol.

By using the primary water-enriched stream as cooling water, the abundance of oxygen caused by aeration in the cooling tower activates the growth of micro-organisms that use dissolved organic constituents in the primary water-enriched  
20 stream as food source.

The evaporation may comprise use of the primary water-enriched stream as make up water to an evaporative cooling tower. The evaporative cooling tower  
25 may be selected from the group including: mechanical-draft cooling towers, natural-draft cooling towers and forced-draft cooling towers.

When using the primary water-enriched stream as cooling water, the linear flow velocity of said water through the equipment being used in the cooling process  
30 must be sufficiently high enough to inhibit deposition of suspended solids in said equipment.

The pH of the primary water-enriched stream should be controlled by addition of an alkali, such as caustic soda, to prevent acid corrosion of metal and/or concrete surfaces that might be exposed to this water.

- 5 One or more suitable additives may be added to the primary water-enriched stream before using it as cooling water to inhibit undesirable effects such as, for example, fouling, corrosion and scaling.

Biological treatment of the secondary water-enriched stream may include aerobic  
10 treatment.

The aerobic treatment method may be the same as is conventionally used for domestic and industrial wastewater treatment.

- 15 The aerobic treatment may include adding nutrients in the form of nitrogen (e.g. urea, ammonia or ammonium salts) and phosphorus (e.g. phosphate salts) containing compounds to accelerate microbiological degradation of the organic carbon-containing constituents. In addition, pH control using alkali compounds such as lime, caustic and soda ash may be required to optimize performance of  
20 the micro-organisms.

A wide range of technologies may be used in the aerobic treatment of the secondary water-enriched stream. Such technologies may be selected from a group including: Activated Sludge processes, High-rate Compact Reactors,  
25 Biological Aerated Filters, Trickling filters, Rotating Biological Contactors, Membrane Bioreactors, and Fluidised Bed reactors. The aerobic production of Single Cell Protein (SCP) has also been successfully developed.

Apart from a water-rich or tertiary water-enriched stream, aerobic treatment  
30 typically yields carbon dioxide and sludge as byproducts. The carbon dioxide

may be released to the environment. The sludge may be incinerated, used as land fill, fertilizer, soil conditioner or as a source of SCP.

5 | The quartic treatment stage may be aimed at removing suspended solids from the water-rich stream produced during biological treatment.

Suspended solid removal may be achieved by methods selected from the group including: sand filtration, membrane separation (e.g. micro- or ultrafiltration), flocculation sedimentation, dissolved air flotation (with or without the use of  
10 flocculants) and centrifugation.

Residual organic species not removed during biological treatment and solids removal may be removed by methods selected from the group including: chemical oxidation using agents such as ozone and hydrogen peroxide,  
15 ultraviolet light generated free radicals and adsorption/absorption processes including activated carbon treatment and organic scavenging resins.

Dissolved salts, originating from secondary treatment (i.e. pH control chemicals, nutrient addition) and/or from the co-treatment of other process effluents, can be  
20 further reduced by methods from the group including: ion exchange, reverse osmosis, nano-filtration and chemical precipitation processes including hot and cold lime softening.

Applications for the highly purified water produced by the method described  
25 above may include its use as boiler feed water and drinking water.

The highly purified water typically has the following characteristics:

Property		
Chemical Oxygen Demand (COD)	mg/l	<50
pH		6,0- 9,0



Total Dissolved Solids (TDS)	mg/l	< 100
Suspended Solids (SS)	mg/l	< 50

Advantages inherent in the purified and highly purified water produced according to the present invention are that the water will contain only a small amount of dissolved solids because the Fischer-Tropsch reaction water is essentially a solids-free stream. The low levels of residual salts in the purified water are a result of controlled addition of chemicals used during the purification process sequence and/or the co-treatment of other dissolved solids containing effluents. The residual salts include Ca, Mg, Na, K, Cl, SO<sub>4</sub>, HCO<sub>3</sub> and CO<sub>3</sub> combinations. The low dissolved solids concentrations in Fischer-Tropsch reaction water can simplify and reduce the cost of the purification process.

#### Detailed Description of the Invention

The invention will now be described by way of the following non-limiting examples with reference to the accompanying drawing.

Figure 1 shows a simplified block diagram of a method 10 according to the present invention including various treatment options.

Fischer-Tropsch reaction water 12 is fed to a distillation column 14 for primary treatment.

Two streams 16 and 18 exit distillation column 14. Stream 16 contains predominantly organic constituents whilst stream 18 is a primary water-enriched stream.

Stream 18 is then fed to a forced draft cooling tower 20 in which the stream 18 is used as make up water for a forced-draft cooling tower. By utilizing stream 18 as cooling water, its volume is reduced by evaporation and the amount of at least

some of the dissolved organic constituents in stream 18 are reduced due to the abundance of oxygen caused by aeration in the cooling tower 20 activating the growth of micro-organisms that use dissolved organic constituents in the primary water-enriched stream 18 as food source.

5

Stream 22 is the blow down or unevaporated water portion (or secondary water-enriched stream) from the cooling tower 20 and is subjected to biological treatment in the form of aerobic digestion 24 which produces sludge 26, carbon dioxide 28 and a tertiary water-enriched stream 30.

10

The next treatment stage involves subjecting the tertiary water-enriched stream 30 to solid-liquid separation 32 during which solids 34 in the form of sludge as well as a stream of purified water 36 are produced.

15 Some of the purified water 36 from the solid-liquid separation 32 stage is subjected to a final treatment stage in the form of membrane separation 38 to yield highly purified water 40 and concentrate 42. Stream 42 contains non-biodegradable organic species, concentrated inorganic salts eg sulphates and chlorides of sodium and calcium as well as elevated concentrations of suspended  
20 solids.

Depending on the final intended use of the purified 36 or highly purified water 40, the minimum water quality requirements are as set out in Table 2 below and the operating conditions of the equipment used in the method as well as suitable  
25 treatment options can be selected accordingly.

30

Table 2 Water Quality – Typical Requirements

	Process Water	Irrigation water	Cooling water	Boiler feed water	Drinking water
COD mg/l	0 - 75		0 - 30	0 - 10	
pH	5 - 10	6.5 – 8.4	6.5 - 8	7-8	6-9
TDS mg/l	0 - 1600	<40	0 - 450	0 - 100	0 - 450
SS mg/l	0 - 25	0 - 50	0 - 5	0 - 3	<20

Having described the basic aspects of the invention, the following example is given to further illustrate a specific embodiment of the invention.

5

**Example: Treatment of Fischer-Tropsch reaction water derived from a cobalt catalyst LTFT process**

After separation of by-products, a water-enriched stream from a LTFT process was degassed at atmospheric pressure. Free hydrocarbons in the water-enriched stream were reduced to 0.01 % (mass %) using a coalescer.

Primary treatment of the thus obtained Fischer Tropsch reaction water was undertaken using distillation. Analysis of the FT acid water bottoms of the distillation column is detailed in Table 3 below. It is apparent that with the exception of trace quantities of methanol, most other non-acid oxygenated hydrocarbons were removed during primary distillation leaving an organic acid enriched or primary water-enriched stream (i.e. 0.072 mass % organic acids) with a pH value of 3.5. The measured Chemical Oxygen Demand (COD) of this effluent was in the order of 800 mg O<sub>2</sub>/l.

Table 3: Typical Composition of LTFT Reaction Water Feed and Acid Water Bottoms During Primary Treatment (Distillation)

Component	Reaction water feed to primary distillation column (mass %)	Acid water – bottoms of primary distillation column (mass %)
Water	97.629	99.840
Acetaldehyde	0.019	0.000
Propionaldehyde	0.002	0.000
Butyraldehyde	0.001	0.000
Acetone	0.007	0.000
MPK	0.001	0.000
Methanol	0.434	0.001
Ethanol	0.369	0.000
Propanol	0.140	0.000
iso-Propanol	0.002	0.000
Butanol	0.056	0.000
Pentanol	0.047	0.000
iso-Pentanol	0.001	0.000
Hexanol	0.019	0.000
Iso-Hexanol	0.001	0.000
Heptanol	0.007	0.000
Other NAC	0.004	0.000
Total NAC	1.106	0.001
Formic acid	0.025	0.025
Acetic acid	0.039	0.040
Propionic acid	0.002	0.002
Butyric acid	0.002	0.002
Other acids	0.006	0.006
Total Acids	0.070	0.072
Other Hydrocarbons	0.011	0.011

- 5 The primary water-enriched stream was fed into an open holding tank at approximately 70°C.

In order to sustain a microbiological population in the primary water-enriched stream, nitrogen in the form of urea and phosphate in the form of phosphoric acid

were added to said stream. The pH of the primary water-enriched stream was thereafter adjusted to 5 using sodium hydroxide.

5 The primary water-enriched stream was then fed to a forced draft cooling tower as make up water. The cooling tower was operated at four cycles of concentration and a 10°C delta T.

Removal of organics (measured as COD) from the primary water-enriched stream in the tower was in the order of 45% with volatile acid removal at about  
10 55%. The COD of the recirculating water in the tower was approximately 1800 mg/l and the concentration of suspended solids was approximately 200 mg/l whilst the pH of the water varied between 6,5 and 7,5.

Corrosion, fouling and scaling in the cooling tower and surrounding heat  
15 exchangers was kept within acceptable limits by applying an appropriate chemical treatment program that included a biodispersant and a scale inhibitor.

The blow down or unevaporated water portion from the cooling tower (secondary water-enriched stream) was then treated in a completely mixed activated sludge  
20 system (aerobic treatment) under the following conditions:

- pH: 7,2 to 7,5
- Dissolved oxygen concentration: >2 mg/l
- Temperature: 35 °C
- 25 ◦ HRT: 30 h
- F/M ratio : 0,2 -0,4 kg COD/kg MLSS.d
- Cell retention time (sludge age) – 13 days
- Feed to recycle ratio: 1 : 2

30 A COD removal efficiency of 91% was achieved and the thus obtained tertiary water-enriched stream had a COD of 160 mg/l. The suspended solid

concentration of the tertiary water-enriched stream was on average about 120 mg/l.

5 The tertiary water-enriched stream was then subjected to sand filtration to reduce its SS concentration to 25 mg/l. The thus obtained purified water has application as a both irrigation water and process cooling water. Sludge produced in the process was incinerated.

10 As an alternative to treatment in an activated sludge system, the blow down or part of the blow down from the cooling tower was diverted to a cross-flow membrane unit fitted with a 0.2  $\mu\text{m}$  polypropylene microfiltration membrane. A permeate flux rate of 70 – 80  $\text{l/m}^2\cdot\text{h}$  was obtained during stable operation of the unit. The water recovery across the unit varied between 75 – 85 %. The resultant COD and SS concentrations in the permeate from the microfiltration unit were  
15 1750  $\text{mg O}_2/\text{l}$  and < 5  $\text{mg/l}$  respectively.

The pH of the purified water from the microfiltration unit was adjusted to 8.5 using sodium hydroxide and the purified water was pumped to a reverse osmosis unit fitted with a high rejection polyamide sea water membrane. A permeate flux rate  
20 of 20 – 25  $\text{l/m}^2\cdot\text{h}$  was obtained during stable operation of the unit. The water recovery across the reverse osmosis unit varied between 80 – 90 %. The unit yielded a highly purified water stream with COD and TDS concentrations of 45 – 50  $\text{mg O}_2/\text{l}$  and 20 – 30  $\text{mg/l}$  respectively.

25 It is to be appreciated that the invention is not limited to any specific embodiment or configuration as herein before generally described or illustrated, for example, rain water or water enriched streams from processes other than Fischer-Tropsch synthesis may be purified according to the method described above.

**Claims:**

1. A process for the production of purified water from Fischer-Tropsch reaction water wherein the purified water is an aqueous stream having a COD of  
5 between 20 and 500 mg/l, a pH of between 6,0 and 9,0, a suspended solids content of less than 250 mg/l and a total dissolved solids content of less than 600 mg/l, and wherein the process includes at least the steps of:-
  - a) a primary treatment stage comprising an equilibrium staged separation process having at least one stage for removing at least a fraction of non-acid  
10 oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
  - b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby reducing the total mass fraction of organic constituents in the unevaporated portion to produce a secondary  
15 water-enriched stream; and
  - c) a final treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the secondary water-enriched stream.
- 20 2. A process for the production of purified water from Fischer-Tropsch reaction water wherein the purified water is an aqueous stream having a COD of between 20 and 500 mg/l, a pH of between 6,0 and 9,0, a suspended solids content of less than 250 mg/l and a total dissolved solids content of less than 600 mg/l, and wherein the process includes at least the steps of:-
  - 25 (a) a primary treatment stage comprising an equilibrium staged separation process having at least one stage for removing at least a fraction of non-acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
  - (b) a secondary treatment stage comprising evaporation of at least a portion of  
30 the primary water-enriched stream thereby reducing the total mass fraction

- of organic constituents in the unevaporated portion to produce a secondary water-enriched stream;
- (c) a tertiary treatment stage comprising biological treatment for removing at least a fraction of dissolved organic carbon from the secondary water-enriched stream to produce a tertiary water-enriched stream; and
- 5 d) a quartic treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the tertiary water-enriched stream.
- 10 3. A process as claimed in claim 1 or claim 2 wherein the non-acid oxygenated hydrocarbons are selected from the group including: acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl-propyl-ketone, methanol, ethanol, propanol, butanol, pentanol, hexanol, and heptanol.
- 15 4. A process as claimed in any one of claims 1 to 3 wherein the dissolved organic carbon is selected from the group including: aldehydes, ketones, alcohols, and organic acids.
- 20 5. A process as claimed in any one of the preceding claims wherein the equilibrium staged separation process for use in the primary treatment stage is selected from the group including: distillation, solvent extraction using liquid solvents, and solvent extraction using liquefied gases.
- 25 6. A process as claimed in any one of the preceding claims wherein the primary treatment stage includes degassing of the Fischer-Tropsch reaction water before further processing in the primary treatment stage to remove compounds having a very low boiling point and dissolved gases from the Fischer-Tropsch reaction water.



7. A process as claimed in any one of the preceding claims wherein the evaporation in step b) takes place at ambient temperature and pressure in a cooling tower.
- 5 8. A process as claimed in any one of the preceding claims wherein the evaporation in step b) takes place by using the primary water-enriched stream as make up water to an evaporative cooling tower.
9. A process as claimed in claim 8 wherein the evaporative cooling tower is  
10 selected from the group including: mechanical-draft cooling towers, natural-draft cooling towers, and forced-draft cooling towers.
10. A process as claimed in any one of claims 2 to 9 wherein the biological treatment of step c) is an aerobic treatment method.
- 15 11. A process as claimed in claim 10 wherein the aerobic treatment method is selected from group including: Activated Sludge processes, Biological Aerated Filters, Trickling filters, Rotating Biological Contactors, High-rate Compact Reactors, Membrane Bioreactors and Fluidised Bed reactors.
- 20 12. A process as claimed in any one of claims 2 to 11 wherein the quartic treatment stage removes suspended solids from the tertiary water-enriched stream produced during biological treatment.
- 25 13. A process as claimed in claim 12 wherein the suspended solid removal is achieved by one or more method selected from the group including: sand filtration, membrane separation, flocculation sedimentation, dissolved air flotation with the use of flocculants, dissolved air flotation without the use of flocculants, and centrifugation.
- 30

14. A process as claimed in claim 13 wherein the membrane separation method includes one or both of microfiltration and ultrafiltration.
15. A process for the production of highly purified water from Fischer-Tropsch reaction water wherein the highly purified water is an aqueous stream having a COD of less than 50 mg/l, a pH of between 6,0 and 9,0, a suspended solids content of less than 50 mg/l and a total dissolved solids content of less than 100 mg/l, and wherein the process includes at least the steps of:-
- 10 a) a primary treatment stage comprising an equilibrium staged separation process having at least one stage for removing at least a fraction of non-acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
- 15 b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby to reduce the total mass fraction of organic constituents in the unevaporated portion to produce a secondary water-enriched stream;
- 20 c) a tertiary treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the secondary water-enriched stream, to produce a tertiary water-enriched stream; and
- (d) a final treatment stage comprising a dissolved salt and organic removal stage for removing at least some dissolved salts and organic constituents from at least a portion of the tertiary water-enriched stream.
- 25 16. A process for the production of highly purified water from Fischer-Tropsch reaction water wherein the highly purified water is an aqueous stream having a COD of less than 50 mg/l, a pH of between 6,0 and 9,0, a suspended solids content of less than 50 mg/l and a total dissolved solids content of less than 100 mg/l, and wherein the process includes at least the
- 30 steps of:-

- a) a primary treatment stage comprising an equilibrium staged separation process having at least one stage for removing at least a fraction of non-acid oxygenated hydrocarbons from the Fischer-Tropsch reaction water to produce a primary water-enriched stream;
  - 5 b) a secondary treatment stage comprising evaporation of at least a portion of the primary water-enriched stream thereby to reduce the total mass fraction of organic constituents in the unevaporated portion to produce a secondary water-enriched stream;
  - c) a tertiary treatment stage comprising biological treatment for removing at  
10 least a fraction of dissolved organic carbon from the secondary water-enriched stream to produce a tertiary water-enriched stream;
  - d) a quartic treatment stage comprising solid-liquid separation for removing at least some solids from at least a portion of the tertiary water-enriched stream to produce a quartic water-enriched stream; and
  - 15 e) a final treatment stage comprising a dissolved salt and organic removal stage for removing at least some dissolved salts and organic constituents from at least a portion of the quartic water-enriched stream.
17. A process as claimed in claim 15 or 16 wherein the non-acid oxygenated  
20 hydrocarbons are selected from the group including: aldehydes, ketones, alcohols, and organic acids.
18. A process as claimed in any one of the claims 15 to 17 wherein the  
25 equilibrium stage separation process for use in the primary treatment stage is selected from the group including: distillation, solvent extraction using liquid solvents, and solvent extraction using liquefied gases.
19. A process as claimed in any one of the claims 15 to 18 wherein the primary  
30 treatment stage includes degassing of the reaction water before further processing in the primary treatment stage to remove compounds having a

very low boiling point and dissolved gases from the Fischer-Tropsch reaction water.

- 5      20. A process as claimed in any one of the claims 15 to 19 wherein the evaporation in step b) takes place at ambient temperature and pressure in a cooling tower.
- 10      21. A process as claimed in claim 20 wherein the evaporative cooling tower is selected from the group including: mechanical-draft cooling towers, natural-draft cooling towers, and forced-draft cooling towers.
- 15      22. A process as claimed in any one of the preceding claims wherein the biological treatment of step c) is an aerobic treatment method.
- 20      23. A process as claimed in claim 22 wherein the aerobic treatment method is selected from group including: Activated Sludge processes, Biological Aerated Filters, Trickling filters, Rotating Biological Contactors, High-rate Compact Reactors , Membrane Bioreactors, and Fluidised Bed reactors.
- 25      24. A process as claimed in any one of the claims 16 to 23 wherein the quartic treatment stage removes suspended solids from the tertiary water-enriched stream produced during biological treatment.
- 30      25. A process as claimed in claim 24 wherein the suspended solid removal is achieved by one or more method selected from the group including: sand filtration, membrane separation, flocculation sedimentation, dissolved air flotation with the use of flocculants, dissolved air flotation without the use of flocculants, and centrifugation.
- 30      26. A process as claimed in claim 25 wherein the membrane separation method includes one or both of microfiltration and ultrafiltration.

27. A process as claimed in any one of claims 16 to 26 wherein residual organic species are removed in the final treatment stage by one or more methods selected from the group including: chemical oxidation, ultraviolet light generated free radicals, adsorption and/or absorption processes.
- 5
28. A process as claimed in claim 27 wherein the adsorption and/ or absorption processes include one or both of activated carbon treatment and the use of organic scavenging resins.
- 10
29. A process as claimed in any one of claims 16 to 28 wherein dissolved salts originating from tertiary treatment and/or from the co-treatment of other process effluents, are reduced in the final treatment stage by one or more method selected from the group including: ion exchange, reverse osmosis, nano-filtration, and chemical precipitation processes.
- 15
30. A process as claimed in claim 29 wherein the chemical precipitation processes are selected from one or both of hot lime softening and cold lime softening.
- 20
31. A process according to the invention for the production of purified water from Fischer-Tropsch reaction water substantially as hereinbefore described or exemplified.
- 25
32. A process of producing purified water from Fischer-Tropsch reaction water including any new and inventive integer or combination of integers, substantially as herein described.
- 30
33. A process according to the invention for the production of highly purified water from Fischer-Tropsch reaction water substantially as hereinbefore described or exemplified.

34. A process of producing highly purified water from Fischer-Tropsch reaction water including any new and inventive integer or combination of integers, substantially as herein described.

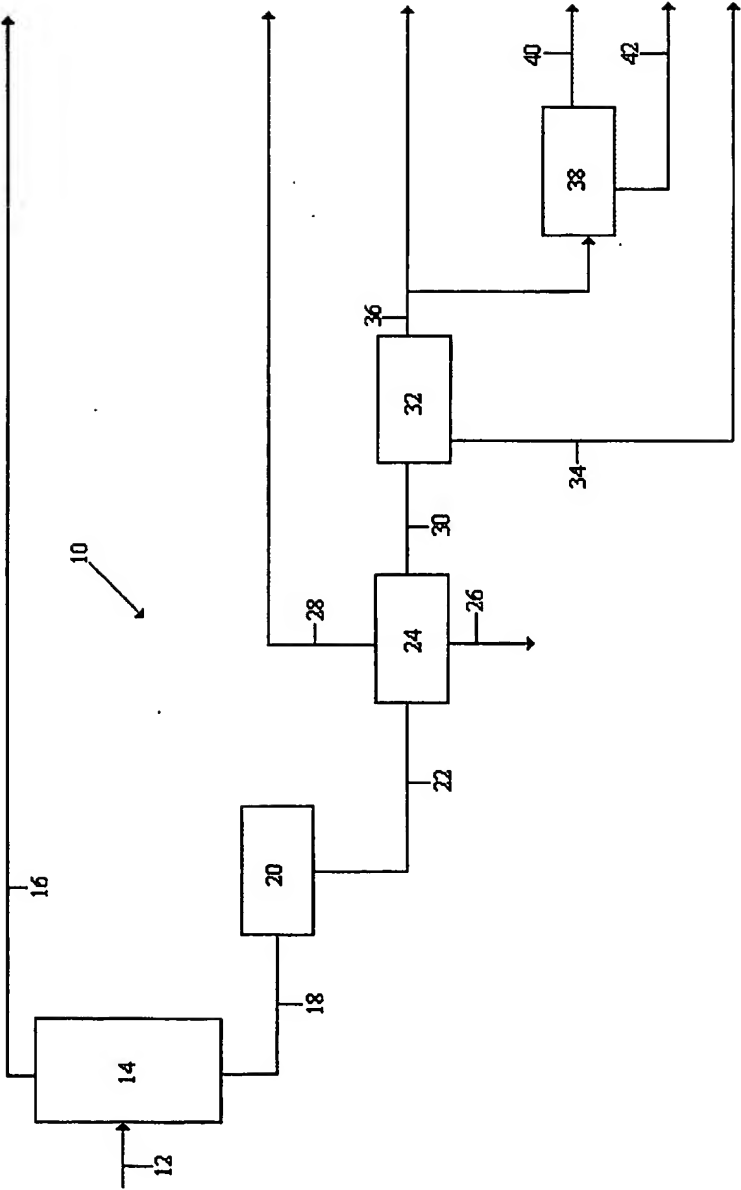


Figure 1

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/ZR 03/00080

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/04 C02F3/00 C02F3/02 C02F9/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 807 027 A (INST FRANCAIS DU PETROL) 5 October 2001 (2001-10-05)  claims 1,3,5-7; figure 1 page 4, lines 10-14 and 20-27 page 6, line 23-31 page 9, line 26 -page 10, column 6 ---	1-6, 10-19, 22-30
A	GB 672 365 A (CITIES SERVICE OIL CO) 21 May 1952 (1952-05-21) claim 1; figure page 1, line 88 -page 2, line 29 --- -/--	1-30

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the International filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

23 October 2003

Date of mailing of the international search report

03/11/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Harf, J



## INTERNATIONAL SEARCH REPORT

International Application No. . . .

PCT/ZA 03/00080

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 683 158 A (BURNSIDE HARVEY E W ET AL) 6 July 1954 (1954-07-06) figures 1,2B column 2, line 3-8 column 3, line 25-29 column 4, line 6-10 column 12, line 18-36 -----	1-30
P,A	WO 03 048272 A (RUSSELL RICHARD ALAN .; ROELOFSE ANDRIES JOHANNES (ZA); SASOL TECHNO) 12 June 2003 (2003-06-12) claim 1; figure 1 page 8, line 30-32 -----	1-30

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/ZA 03/00080

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 31-34  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

## 1. Claims: 1,3-9,15,17-23

a process for the production of purified water from Fischer-Tropsch reaction water wherein the purified water has a COD of less than 500 mg/l, a pH of between 6.0 and 9.0, a suspended solids content of less than 250 mg/l and a total dissolved solids content of less than 600 mg/l and comprising:

- (i) a primary treatment stage to remove at least a fraction of non-acid oxygenated hydrocarbons in an equilibrium staged separation process;
- (ii) a secondary treatment stage to reduce the total mass fraction of organic constituents of the primary water-enriched stream by evaporation of at least a portion of it;
- (iii) a tertiary treatment stage comprising solid-liquid separation to remove at least some solids from at least a portion of the secondary water-enriched stream.

## 2. Claims: 2-14,16-30

a process for the production of purified water from Fischer-Tropsch reaction water wherein the purified water has a COD of less than 500 mg/l, a pH of between 6.0 and 9.0, a suspended solids content of less than 250 mg/l and a total dissolved solids content of less than 600 mg/l and comprising:

- (i) a primary treatment stage to remove at least a fraction of non-acid oxygenated hydrocarbons in an equilibrium staged separation process;
- (ii) a secondary treatment stage to reduce the total mass fraction of organic constituents of the primary water-enriched stream by evaporation of at least a portion of it;
- (iii) a tertiary treatment stage comprising a biological treatment for removing at least a fraction of dissolved organic carbon from the secondary water-enriched stream;
- (iv) a quartic treatment stage comprising solid-liquid separation to remove at least some solids from at least a portion of the tertiary water-enriched stream.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 31-34

Present claims 31-34 relate to an extremely large number of possible methods.. In fact, the claims contain so many options that a lack of clarity and conciseness within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear and concise, namely the process for producing purified water from Fischer-Tropsch reaction water by (i) removing non-acid hydrocarbons from the reaction water in an equilibrium staged separation stage; (ii) reducing the total mass fraction of organic constituents by evaporation of the primary water-enriched stream and (iii) removing solids from the secondary water-enriched stream in a final solid-liquid separation stage (claims 1, 2, 15 and 16).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/ZA 03/00080

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2807027	A	05-10-2001	FR 2807027 A1	05-10-2001
			AU 3140201 A	04-10-2001
			US 6462097 B1	08-10-2002
			ZA 200102539 A	30-09-2002
-----				
GB 672365	A	21-05-1952	NONE	
-----				
US 2683158	A	06-07-1954	NONE	
-----				
WO 03048272	A	12-06-2003	WO 03048272 A1	12-06-2003
-----				